

# **Growth and Properties of Silicon Filaments for Photovoltaic Applications**

T.F. Ciszek and T.H. Wang

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National Renewable Energy Laboratory  
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Golden, Colorado 80401-3393  
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# GROWTH AND PROPERTIES OF SILICON FILAMENTS FOR PHOTOVOLTAIC APPLICATIONS

T. F. Ciszek and T. H. Wang  
National Renewable Energy Laboratory, Golden, CO 80401 USA

## ABSTRACT

Thin silicon filaments were grown from the melt by three different methods: (a) RF-heated float-zone pedestal growth of high-purity, dislocation-free, single-crystal filaments, (b) growth of  $\langle 112 \rangle$  axis, (111) face, dendrite filaments at high pulling rates from a supercooled melt in a quartz crucible, and (c) capillary die growth of thin-walled, small-diameter Si tube-filaments with high ratio of surface area to volume and concomitant device structure advantages. Minority-carrier lifetime  $\tau$  was used to assess the filaments. For the three growth methods listed above, values as high as 660  $\mu\text{sec}$ , 53  $\mu\text{sec}$ , and 42  $\mu\text{sec}$  were observed, respectively. Thin silicon filaments with good crystallographic perfection, grown at high speeds, may be useful as active semiconductor elements in multiple linear-concentrator-array PV systems and in other optoelectronic applications.

## INTRODUCTION

Small-diameter silicon filaments (SiFi's) with good crystallographic perfection can be grown at high speeds and may be useful as active semiconductor elements in multiple linear-concentrator-array PV systems. Other potential applications might include infrared light guides, semiconductor delay lines, and silicon probe tips. This paper discusses three approaches for SiFi growth, each with a particular characteristic advantage: (a) radio frequency-(RF)-heated float-zone pedestal (FZP) SiFi growth; (b) growth of  $\langle 112 \rangle$  axis, (111) face, dendrite SiFi's from a supercooled melt in a crucible; and (c) thin-walled, small-diameter, tubular SiFi growth from a capillary shaping die.

FZP growth is an extension of the well-known Dash method [1] for growing a "neck" from the seed crystal before enlarging the diameter of Si float-zoned (FZ) or Czochralski (CZ) crystals, to produce dislocation-free crystals. Hence, the main advantage of the FZP process is that dislocation-free filaments can easily be grown and the purity is high. The main limitation to minority-charge carrier lifetime is the fast cooling rate relative to that of large-diameter crystals, because of the high growth speed. The calculated growth speed limit [2] for FZP SiFi's is:

$$v_{\max} = (1/L\rho_m)(\sigma\epsilon K_m T_m^5/r)^{1/2},$$

where  $L$  is the latent heat of fusion,  $\rho_m$  is the density of the SiFi at the melting temperature,  $\sigma$  is the Stefan-Boltzmann constant,  $\epsilon$  is the surface emissivity of the SiFi,  $K_m$  is the thermal conductivity of the SiFi at the melting temperature  $T_m$ , and  $r$  is the SiFi radius. For a 1-mm-diameter SiFi,  $v_{\max} = 4$  m/h.

Dendrites grow from a supercooled melt in a specific orientation that allows rapid nucleation, namely  $\langle 112 \rangle$ . Thus, the characteristic advantage of dendrite growth is extraordinarily high growth speeds (proportional to the amount of supercooling,  $\Delta T$  [3]), and sustainable rates on the order of 18 m/h are thought to be feasible. The low surface free-energy of (111) planes provides a narrow ribbon with flat faces, if the growth is propagated in a continuous manner. The SiFi's produced in this manner are single crystal, except for twins in the plane of the narrow ribbon. Hence, reasonably high  $\tau$  is expected.

Tubular SiFi's grown by a capillary-action shaping technique possess a high ratio of surface area to volume and concomitant device structure advantages. In addition, geometrical shaping is provided by the graphite capillary die. The wall thickness is easily affected by either pulling speed or system temperature. For example, pioneering work [4] on the growth of small silicon tubes showed there is a linear dependence of wall thickness on temperature of  $-0.10$  mm/ $^{\circ}\text{C}$  and that tubes could be grown over a wide operating range of  $\pm 3^{\circ}\text{C}$ .

## FILAMENT GROWTH

### Float-Zone Pedestal Silicon Filament Growth

FZP SiFi's were grown from 5-mm-diameter Si feed rods using a custom RF coil with a water-cooled shorting ring below the coil to limit the RF field below the melting interface and to establish a well-defined melting interface. Growth was initiated on thin  $\langle 111 \rangle$ ,  $\langle 100 \rangle$ , or  $\langle 115 \rangle$  seeds that were immersed into the top surface of the dome-shaped melt atop the feed rod. Growth was stabilized at a steady-state power input and pulling rate. We explored pulling rates in the range 12-30 mm/min, and grew filaments with diameters from 0.3 mm to over 2 mm. The growth zone for a 0.7-mm-diameter filament is shown in Fig. 1, and Fig. 2 shows a group of filaments of various

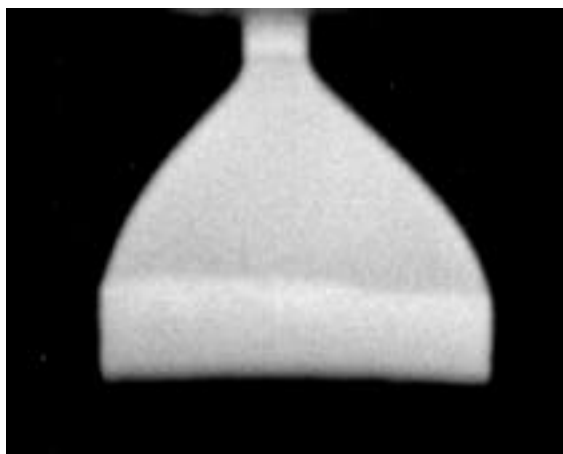


Fig. 1. Photograph of a 0.7-mm-dia. FZP SiFi growing from a 5-mm-dia. feed rod.

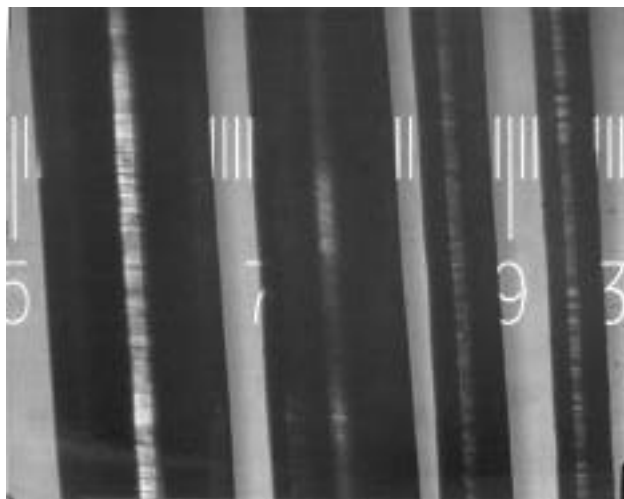


Fig. 2. Several dislocation-free silicon filaments grown by the FZP method. The smallest scale division is 0.1 mm.



Fig. 3. Hot-zone components for Si dendrite growth. The photo width represents 167 mm.

sizes. The smallest scale marks in Fig. 2 represent 0.1 mm. Of course, it is also possible (and easier) to grow larger-diameter filaments or rods. Rods of 5-mm diameter are routinely grown and used as substrates for chemical vapor deposition of polycrystalline-silicon feed stock, for example. The maximum filament length we have grown is 49 cm. Continuous growth should be feasible with a properly designed pulling and guide mechanism.

### Silicon Dendrite Growth

Dendrites were grown from a supercooled melt contained in a 2-cm-dia. quartz crucible. A graphite susceptor surrounding the crucible was RF-heated at 2.1 MHz frequency. Heat shields were used to help maintain a cool center and warmer periphery in the melt. The hot-zone components are shown in Fig. 3. They consist of a 52-mm-I.D. by 34-mm-tall RF coil with a bottom lip, a 50-mm-O.D. by 43 mm tall quartz cup that sits on the coil lip, a 31-mm-I.D. by 46-mm-O.D. by 36-mm-tall susceptor that rests in the cup, a quartz crucible that sits in the susceptor, and two graphite shields with a separator ring.

Previously grown dendrites were used as seeds. The seed/melt equilibrium was established, and then power was reduced to establish supercooling. After a time interval, pulling was begun. Several resultant dendrite widths are shown in Fig. 4. The smallest scale marks again represent 0.1 mm. We have not yet explored the range of feasible pulling speeds, but expect speeds greater than several hundred mm/min to be feasible, because growth in the dendritic configuration along the  $\langle 112 \rangle$  direction has reentrant nucleation sites that promote unusually rapid solidification.

### Silicon Tubular Filament Growth

Tubular SiFi's were grown from high-density graphite dies with an annular capillary channel. The Si melt was

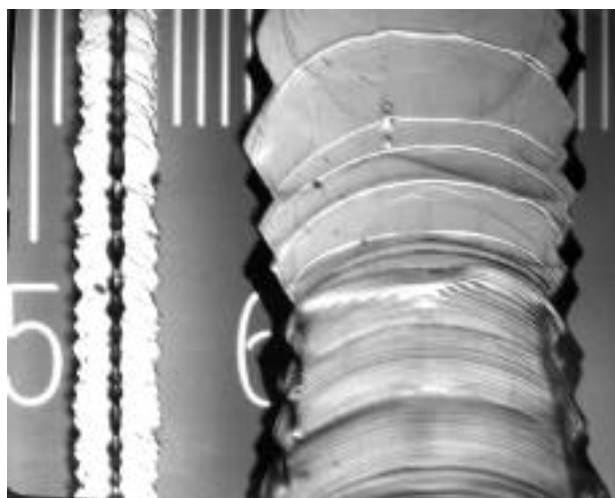


Fig. 4. Examples of dendrites grown from a supercooled melt. The smallest scale division is 0.1 mm.

held in a quartz crucible within a graphite susceptor. RF heating at 360 kHz was used. The ambient was high-purity argon. Growth was initiated with a thin Si seed at one point on the die channel and allowed to spread around and close the tube. Details of growth were similar to those for the first-reported silicon tube growth in 1975 [4]. A growing tube is shown in Fig. 5. Wall thickness is determined by temperature and pull speed, and various diameters can be obtained by die geometry. A segment of a 6-mm-diameter tube is depicted in Fig. 6.

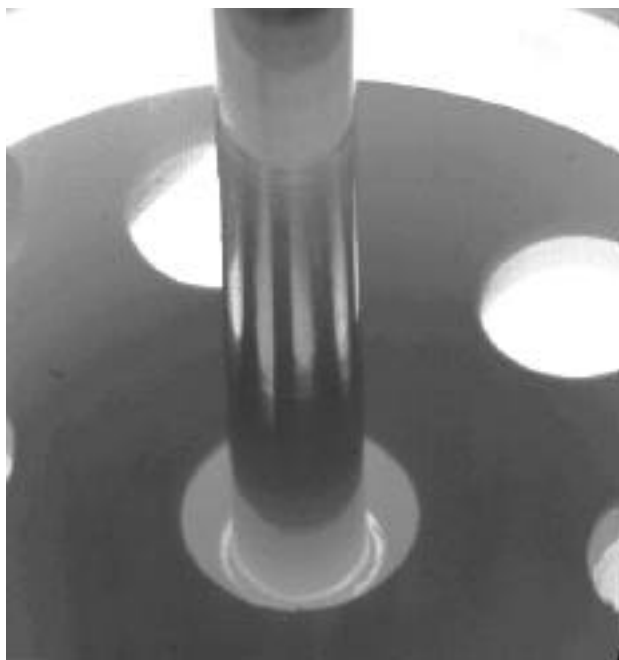


Fig. 5. Growth of a 6-mm-diameter tubular SiFi from a graphite capillary shaping die.



Fig. 6. A 6-mm-diameter silicon tube with approximately 0.7-mm wall thickness grown from a capillary die.

## MINORITY-CARRIER LIFETIME CHARACTERIZATION

Minority-carrier DC photoconductive decay (PCD) lifetime measurements by the ASTM F28-75 method were used to assess the filaments. The filament surface was passivated by sealing the filament in a glass tube filled with saturated iodine-methanol solution, with both filament ends protruding from the seals. Silver paint was used to contact the portions of the filament outside each sealed tube end, and the ends were masked from incident light.

A number of different SiFi's produced by each of the three growth techniques were measured. The highest lifetimes observed for the three growth methods are shown in Table I.

Table 1. Highest Minority-Carrier Lifetimes Observed for Each of Three Si Filament Growth Methods

Filament growth method	Highest Lifetime ( $\mu$ s)
Float-zone pedestal	660
Dendrite pulling	53
Capillary die growth of tubes	42

## DISCUSSION AND CONCLUSIONS

Silicon filaments were grown by three methods. Float-zone pedestal growth results in filaments with the highest minority-carrier lifetimes (660  $\mu$ s), which is reasonable because the filaments can be made dislocation-free and the purity level is high because no crucible or other foreign contact is made to the melt. The dendrite filament lifetime is an order of magnitude lower, but still in a range of interest for PV devices. These filaments may contain dislocations and stress centers that lower the lifetime. Also, the higher solidification rates, and hence, cooling rates, cause lifetime degradation [5]. Still lower are the lifetimes of silicon tube filaments. This is a consequence of the grain-boundary defects and dislocations in the multicrystalline tubes.

The minority-carrier lifetimes resulting from all of the filament growth methods are adequate for consideration in linear concentrators, and some of the growth rates may be feasible for such applications. The growth rates potentially achievable for dendrites are particularly attractive. The geometry of tubes, with access to the interior wall surface, could be beneficial for filament device design needs in linear concentrators.

Single-crystal FZP SiFi's may have additional semiconductor applications as well, such as infrared light guides, high-speed time delay devices, and silicon probe tips. They have been grown in lengths up to 49 cm in our present apparatus, but longer filaments should be feasible with appropriate pulling and guidance mechanisms.

There do not appear to be fundamental limitations to semicontinuous growth for any of the three methods. So far, widths or diameters in the range 0.3 mm to 6 mm have been grown. It is unlikely that thinner ones would be required for PV use.

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## REFERENCES

- [1] W. C. Dash, *J. Appl. Phys.* **30** (1959) 459.
- [2] T.F. Ciszek, *J. Appl. Phys.* **47** (1976) 440.
- [3] R.L. Longini, A.I. Bennett, and W.J. Smith, *J. Appl. Phys.* **31** (1960) 1204.
- [4] T.F. Ciszek, *phys. stat. sol. (a)* **32** (1975) 521.
- [5] T. F. Ciszek, Tihu Wang, T. Schuyler, and A. Rohatgi, *J. Electrochem. Soc.* **136** (1989) 230.